

TECHNICAL REPORT BRL-TR-3094

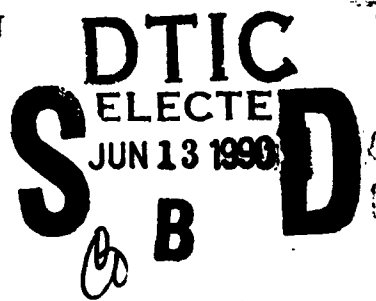
AD-A222 622

**BRL**

EXCIMER LASER FRAGMENTATION STUDIES  
OF SELECTED OXIMES:  
NASCENT OH INTERNAL ENERGY DISTRIBUTIONS  
AND THE SEARCH OF H<sub>2</sub>CN FLUORESCENCE

ROSARIO C. SAUSA  
WILLIAM R. ANDERSON  
ANDRZEJ W. MIZIOLEK  
PAUL J. DAGDIGIAN

MAY 1990



APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

U.S. ARMY LABORATORY COMMAND

BALLISTIC RESEARCH LABORATORY  
ABERDEEN PROVING GROUND, MARYLAND

90 06 12 086

## NOTICES

Destroy this report when it is no longer needed. DO NOT return it to the originator.

Additional copies of this report may be obtained from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The use of trade names or manufacturers' names in this report does not constitute indorsement of any commercial product.

UNCLASSIFIED

## REPORT DOCUMENTATION PAGE

Form Approved  
GSA No. 0704-0100

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0100), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 1990		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE EXCIMER LASER FRAGMENTATION STUDIES OF SELECTED OXIMES: NASCENT OH INTERNAL ENERGY DISTRIBUTIONS AND THE SEARCH OF H <sub>2</sub> CN FLUORESCENCE				5. FUNDING NUMBERS  11L61102AH43	
6. AUTHOR(S) Rosario C. Sausa, William R. Anderson, Andrzej W. Miziolek, Paul J. Dagdigian*					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)				8. PERFORMING ORGANIZATION REPORT NUMBER  BRL-TR-3094	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Ballistic Research Laboratory ATTN: SLCBR-DD-T Aberdeen Proving Ground, MD 21005-5066				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES *The Johns Hopkins University Published in the Journal of Physical Chemistry, Vol. 93, No. 16, 1989					
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Excimer laser excitation (193 nm) of formaldoxime (H <sub>2</sub> CN-OH) or the methylated homologs, R <sub>1</sub> R <sub>2</sub> CN-OH where R <sub>1</sub> , R <sub>2</sub> = H or CH <sub>3</sub> , results in dissociation. The upper limit for the quantum yield of fluorescence of the R <sub>1</sub> R <sub>2</sub> CN is estimated to be between 1-10% depending on the precursor used. The OH companion radical was probed by laser induced fluorescence (LIF) utilizing the A-X (2-1) and (1,0) bands near 34700 cm <sup>-1</sup> , and the nascent rotational, vibrational, and ground electronic state spin-orbit distributions determined. No laser induced fluorescence of the R <sub>1</sub> R <sub>2</sub> CN radical could be observed upon irradiation in the regions where the radicals are known to absorb, 280 to 295 nm. From the nascent OH product distributions, we calculate that only 2.5 Kcal/mole of the excess energy appears as OH product internal energy, thus leaving about 80 Kcal/mole to be divided between the R <sub>1</sub> R <sub>2</sub> CN fragment and translation. We, therefore, conclude that it is highly likely that the upper states of these radicals probed in the 280 to 295 nm region are predissociative. (S)					
14. SUBJECT TERMS Excimer Laser, Formaldoxime, Methyleneamidogen, Laser-Induced, Fluorescence, Spin-Orbit, Hydroxyl, Formaldazine, Acetaldoxime, Dissociation-Energy, Electronic State				15. NUMBER OF PAGES 29	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL		

NSN 7540-01-280-5500

UNCLASSIFIED

Standard Form 298 (Rev. 2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

INTENTIONALLY LEFT BLANK.

# TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.....	1
II. EXPERIMENTAL SECTION.....	2
III. RESULTS AND DISCUSSION.....	4
A. Fragmentation Energetics.....	4
B. OH Fragment Internal State Distributions.....	5
C. Search for H <sub>2</sub> CN Fluorescence.....	6
D. Detection of CN.....	10
IV. CONCLUSION.....	11
ACKNOWLEDGMENT.....	13
REFERENCES.....	15
DISTRIBUTION LIST.....	19

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	20



INTENTIONALLY LEFT BLANK.

## I. INTRODUCTION

There has been considerable interest in the development of sensitive laser spectroscopic probes for the detection of trace transient species in combustion environments.<sup>1,2</sup> Laser-induced fluorescence has been utilized for the observation of a number of free radical combustion species.<sup>3</sup> In this paper, we describe our attempt to observe laser-induced fluorescence of the methyleneamidogen radical,  $\text{H}_2\text{CN}$ , which is prepared by excimer laser photodissociation of formaldoxime [ $\text{H}_2\text{CNOH}$ ]. We have also investigated the photodissociation of the methylated homologs of formaldoxime, namely acetaldoxime [ $\text{CH}_3\text{CHNOH}$ ] and acetoxime [ $(\text{CH}_3)_2\text{CNOH}$ ]. We also report the internal state distribution of the companion photofragment, hydroxyl, for these three precursors.

Methyleneamidogen was first observed by Cochran, et al.,<sup>4</sup> by ESR spectroscopy in an argon matrix and has been observed in other experiments by the same technique.<sup>5-9</sup> The ultraviolet absorption spectrum of  $\text{H}_2\text{CN}$  was first observed through flash photolysis of formaldazine [ $(\text{H}_2\text{CN})_2$ ]<sup>10-12</sup> and subsequently in the photolysis of formaldoxime.<sup>13</sup> The observation of the same bands from these two precursors supported their assignment to  $\text{H}_2\text{CN}$ , and deuterium-substitution studies confirmed the presence of two hydrogen atoms in the molecule.<sup>10</sup> No rotational structure could be resolved in these bands. Recently, the infrared spectra of  $\text{H}_2\text{CN}$  and its deuterated counterparts have been observed by Jacox in an argon matrix.<sup>14</sup> All the vibrational bands have been assigned. The ultraviolet absorption spectrum was also observed, with only a small matrix shift. The methylated homologs of methyleneamidogen, namely  $\text{CH}_3\text{CHN}$  and  $(\text{CH}_3)_2\text{CN}$ , were also observed in the gas phase by flash photolysis, in this case, of the precursors acetaldazine [ $(\text{CN}_3\text{CHN})_2$ ] and dimethylketazine [ $((\text{CH}_3)_2\text{CN})_2$ ].<sup>12</sup>

Methyleneamidogen is believed to be formed in the early stages of the decomposition of nitramines, a class of important high-energy molecules.<sup>15,16</sup> Using ESR spectroscopy, Morgan and Beyer<sup>9</sup> observed  $\text{H}_2\text{CN}$ , along with nitrogen dioxide, as one of the species present in the vapors produced by the slow pyrolysis of cyclotetramethylenetetranitramine (HMX) near its melting point. The electron spin resonance spectrum they obtained for the matrix-deposited vapors from this pyrolysis was essentially identical to spectra of  $\text{H}_2\text{CN}$  obtained by other methods.<sup>4-8</sup> This transient molecule is also believed to be formed by the dissociation of methylenenitramine [ $\text{CH}_2\text{NNO}_2$ ], which has been experimentally identified as a primary decomposition product in the molecular beam infrared multiphoton dissociation of cyclotrimethylenetri-nitramine (RDX).<sup>17</sup> Methyleneamidogen may also be important as an intermediate in the reaction of hydrogen atoms with HCN.<sup>18</sup>

Further studies of the role of methyleneamidogen in nitramine decomposition would clearly benefit from a sensitive diagnostic tool for the detection of this species. The most prominent features in its electronic absorption spectrum occur near 280 nm.<sup>10-13</sup> There actually appear to be two electronic transitions occurring in this spectral region.<sup>11,19</sup> Quantum chemical calculations have also been carried out in order to estimate vertical excitation energies.<sup>19</sup> These calculations give a reasonable explanation of the electronic spectrum of this radical and provide assignments for the electronic states involved in the bands near 280 nm.

In this paper, we report a search for laser induced-fluorescence of methyleneamidogen and its methylated homologs upon excitation of the bands previously observed by flash photolysis. In view of the fact that no rotational structure was observed using a 10.7 meter spectrograph with  $0.3 \text{ cm}^{-1}$  spectral resolution,<sup>11</sup> the excited states of  $\text{H}_2\text{CN}$  may in fact be predissociated. Jacox<sup>14</sup> observed that the ultraviolet absorptions of a matrix-isolated sample decreased upon exposure to light from a medium-pressure mercury arc, while they remained unchanged when the sample was irradiated with light from an arc of wavelengths greater than 280 nm. If the excited state were strongly predissociated, it would, of course, lead to a negligible fluorescence quantum yield. It is interesting in this regard to make the comparison with the isoelectronic formyl radical,  $\text{HCO}$ . Most of the excited levels of  $\text{HCO}$  are diffuse, except for those with  $K'=0$ .<sup>20</sup> A laser optogalvanic study<sup>21</sup> revealed, in fact, a strong variation of the linewidth in the  $\text{A}^2\text{A}''$  (0,9,0)  $K'=0$  manifold. In spite of this predissociation,  $\text{HCO}$  has been successfully detected by fluorescence excitation in the  $\text{A}^2\text{A}''$  (0,9,0)- $\tilde{\text{X}}^2\text{A}'$  (0,0,0) band.<sup>22,23</sup> More recently, the formyl radical has been detected in both a cell<sup>24</sup> and in a flame<sup>25</sup> by two-photon-resonant multiphoton ionization near 390-400 nm via its 3s and 3p Rydberg states. In view of the importance of developing a diagnostic for  $\text{H}_2\text{CN}$ , it was deemed worthwhile to investigate whether fluorescence could be observed with this molecule upon excitation of its known ultraviolet band systems.

We have chosen in this study to prepare methyleneamidogen by excimer laser photolysis of formaldoxime since the other photofragment is the hydroxyl radical, which is easily detected by fluorescence excitation. Formaldoxime exists at room temperature as a polymer and must be heated to produce the monomeric vapor.<sup>26</sup> Detection of the hydroxyl radical allows indirect verification of the presence of the oxime precursor and also provides a way to estimate our detection sensitivity for methyleneamidogen. Because of the difficulty in producing formaldoxime vapor, we have also investigated the photodissociation of its methylated homologs, acetaldoxime [ $\text{CH}_3\text{CHNOH}$ ] and acetoxime [ $(\text{CH}_3)_2\text{CNOH}$ ]. These precursors are expected to yield  $\text{CH}_3\text{CHCN}$  and  $(\text{CH}_3)_2\text{CN}$ , whose absorption spectra have been previously observed by flash photolysis of the corresponding azines.<sup>12</sup> These molecules were also investigated in the hope that their predissociation rate may be significantly less than that of  $\text{H}_2\text{CN}$ . Finally, the photodissociation of formaldazine and acetaldazine was also briefly studied.

## II. EXPERIMENTAL SECTION

These experiments were carried out in a large vacuum chamber normally used for molecular beam scattering studies.<sup>27</sup> The photolysis source was an excimer laser (Lambda Physik EMG101MSC) usually operated at 193 nm with ArF; typical pulse energies of the unpolarized output were 10-20 mJ in a 1 cm x 3 cm rectangular area at the photolysis zone. A few experiments with acetaldazine precursor were carried out at 248 nm with KrF. The tunable ultraviolet probe laser beam, obtained by frequency doubling the output of a Nd:YAG pumped dye laser (Quantel), crossed at right angles to the excimer laser beam along the long dimension. Typical probe pulse energies at the apparatus were 200  $\mu\text{J}$  in a 4 mm diameter beam for laser fluorescence detection of OH in the  $\text{A}^2\Sigma^+ - \text{X}^2\Pi$  (1,0) and (2,1) bands at 280-290 nm. Slightly higher power (500-800  $\mu\text{J}$ ) was employed in the search for fluorescence from  $\text{H}_2\text{CN}$  and



its homologs. Fluorescence detection of CN through excitation of its  $B^2\Sigma^+ - X^2\Sigma^+$  (0,0) band near 388 nm was accomplished by mixing the dye laser output with the residual 1.06  $\mu\text{m}$  Nd:YAG fundamental. The incident pulse energy of the probe radiation was approximately 100  $\mu\text{J}$ .

Fluorescence excited by the probe laser was collected with a 3-lens telescope and was detected with a photomultiplier (EMI 9813QB), whose output was directed to a gated integrator (Stanford Research Systems). For experimental convenience, the fluorescence telescope has a  $90^\circ$  bend in it. To reduce the scattered light background, a dichroic mirror, with reflectivity peaked over 300-350 nm, was used to make this bend. Below 300 nm, the reflectivity dropped rapidly, reaching 50% at 285 nm. For fluorescence detection of CN, the dichroic mirror was replaced with an aluminized one, and excimer laser scattered light was eliminated with the insertion of a 390 nm center wavelength, 10 nm FWHM filter. In many runs, excitation spectra were acquired under computer control (DEC LSIP-11/23), and the spectra were stored on magnetic diskettes for later analysis on another laboratory computer (Apple Macintosh).

The precursors acetaldoxime and acetoxime were obtained from Aldrich Chemicals. The stated purities were 95 and 98%, respectively. Acetaldazine was synthesized by the reaction of acetaldehyde and hydrazine hydrate according to the procedure of Curtius and Zinkeisen.<sup>28</sup> Checks of the infrared and mass spectra against literature infrared<sup>29</sup> and mass<sup>30</sup> spectra were made to insure the identity of the product. The purity of the product was found to be >98%.

Formaldazine polymer was prepared simply by the addition of formaldehyde to hydrazine hydrate using the procedure of Pulvermacher.<sup>31</sup> The alternative procedure of Hofmann and Storm<sup>32</sup> yields a ring compound, tetraformaltrisazine,  $\text{C}_4\text{H}_{12}\text{N}_6$ , rather than the desired polymer of formula  $(\text{C}_2\text{H}_4\text{N}_2)_n$ .<sup>33</sup> A check of the elemental composition (analytical physical measurements performed by E.I. duPont de Nemours and Company) of our product showed the correct elemental stoichiometry. An infrared spectrum of the polymeric sample was also taken and, in general, agreed with literature spectra of the monomer deposited in a low-temperature matrix.<sup>34,35</sup>

Formaldoxime was synthesized by the procedure of Scholl.<sup>26</sup> The identity and purity of the solid product was checked by infrared and gas chromatograph/mass spectra. Unfortunately, the only infrared spectrum available in the literature is for the gas phase monomer.<sup>36</sup> Also, no literature mass spectrum could be found. However, our observed mass spectrum exhibits approximately the fragmentation pattern expected for  $\text{H}_2\text{CNOH}$ , and the physical properties match known values.

Two types of photodissociation experiments were carried out for the study of both nascent and thermalized products. In the former, the vacuum chamber was evacuated with a baffled diffusion pump. Typical pressures for the precursors were 2-5 mTorr, with pump/probe delays of 2-4  $\mu\text{sec}$ . For the study of thermalized products, the chamber was evacuated with a roughing pump, and nitrogen was added to give a total pressure of 0.6-1 Torr; pump/probe delays were 4-50  $\mu\text{sec}$  and usually greater than 20  $\mu\text{sec}$ .

Acetaldoxime, acetoxime, and acetaldazine, which are monomeric precursors, were admitted into the vacuum chamber by means of a needle valve on an evacuated flask containing the degassed material. Under normal conditions (298 K and 1 atm), formaldazine exists as a solid polymer, while formaldoxime is a solid trimer. In our first experiments, the desired monomeric precursors were obtained by depolymerization of the solids in a heated crucible located just under the photolysis/detection zone. This arrangement generated a significant amount of particulate material, which led to laser scattering that interfered with the taking of laser fluorescence excitation spectra. The problem was exacerbated when an inert diluent was added to the chamber (even at only 1 Torr pressure) because the buoyancy of the diluent gas caused a large amount of particulates to float in the laser beams, or the condensation rates of the generated vapors were affected.

To avoid the light scattering problem, we first attempted to make monomeric formaldoxime liquid, as has been done before.<sup>13,26,36</sup> We found that the best way to handle the gaseous formaldoxime monomer was to depolymerize the solid polymer in a test tube and inject it directly through a long, mildly heated section of metal tubing directly into the photolysis chamber. This procedure avoids the formation of particulates in the chamber. Also, there is very little decomposition because the temperature required is much lower than for formation of the liquid. We found that a depolymerization temperature of 80-90°C produced a pressure of several mTorr in the chamber with the pumps on. This is an adequate amount to perform photolysis experiments.

We did not devise a very satisfactory technique to inject formaldazine monomer into the chamber. Use of a technique similar to that which worked well for formaldoxime (depolymerization in a heated sidearm to the chamber) was thought to be difficult because the depolymerization temperature (ca. 200-220°C<sup>10,11</sup>) is high enough to cause materials problems since the heated components would be exposed to room air. However, in retrospect, this technique might work well because a lower temperature might still be sufficient to produce several mTorr of monomer. (Lower pressures of monomer are required in these experiments than were used in the flash photolysis experiments.<sup>10-14</sup>) In any case, it is clearly probable that the formaldazine monomer could be produced nicely in the photolysis chamber by heating a sidearm contained under vacuum. Such apparatus was not readily available to us. Therefore, most of the experiments on azines were performed with acetaldazine.

### III. RESULTS AND DISCUSSION

#### A. Fragmentation Energetics

There is considerable uncertainty in the  $R_1R_2CN-OH$  bond dissociation energy for the oximes. The bond dissociation energy for formaldoxime ( $R_1 = R_2 = H$ ) can be estimated by using its heat of formation ( $\Delta H_{f,298}^0 = 0$  kcal/mole) derived from bond additivity considerations by Benson and O'Neal<sup>37</sup> and the  $H-HCN$  binding energy (19 kcal/mole) calculated by Bair and Dunning<sup>18</sup> for the  $H_2CN$  species. With the aid of the well-determined heats of formation of  $H$  and  $HCN$ ,<sup>38</sup> we estimate a bond energy of 74 kcal/mole for formaldoxime. The Bond-Additivity-Corrected Moller-Plesset fourth order perturbation theory (BAC-MP4) method has been used to calculate the thermochemistry of a number of combustion species.<sup>16</sup> Using the BAC-MP4 values<sup>39</sup> for  $\Delta H_{f,298}^0$  of  $H_2CNOH$  and

H<sub>2</sub>CN (5.1 and 58.9 kcal/mole, respectively), we obtain a H<sub>2</sub>CN-OH bond energy of 63.0 kcal/mole, which is in moderate agreement with the previous cruder estimate.

We would expect methylation not to change drastically the R<sub>1</sub>R<sub>2</sub>CN-OH bond energy. Benson and O'Neal<sup>37</sup> estimated a value of 48.4 kcal/mole for acetaldoxime (R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H) from available experimental unimolecular decay kinetic data. This value seems quite low in light of the estimates for formaldoxime. Indeed, Benson and O'Neal questioned the validity of the experimental data. We can obtain another value using their estimated<sup>37</sup>  $\Delta H_{f298}^0$  for acetaldoxime (-7.3 kcal/mole) and a BAC-MP4 value<sup>39</sup> for CH<sub>3</sub>CHN (50.1 kcal/mole). We obtain a CH<sub>3</sub>CHN-OH bond energy of 66.6 kcal/mole, which is quite similar to that for formaldoxime. At present, there is no information on acetoxime (R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>); however, we expect a similar bond energy.

The ultraviolet spectra of the oximes contain two absorption regions, a weak diffuse band near 210-213 nm and an intense band with a maximum below 190 nm.<sup>11</sup> Accordingly, our photodissociation studies were carried out only with an ArF excimer laser (193 nm) as the photolysis light source. This implies that there is approximately 85 kcal/mole of energy available to the photofragments, if a R<sub>1</sub>R<sub>2</sub>CN-OH bond energy of 63 kcal/mole is assumed.

#### B. OH Fragment Internal State Distributions

The OH product was observed by laser fluorescence excitation in the A<sup>2</sup>Σ<sup>+</sup> - X<sup>2</sup>Π (1,0) and (2,1) bands. These particular bands were chosen since they lie very close to the wavelengths of the absorptions previously observed for H<sub>2</sub>CN and its homologs. The dependence of the OH fluorescence signals for several lines was investigated as a function of excimer laser pulse energy. On a log-log plot the slope was found to equal 1.25 ± 0.1. This is roughly consistent with a one-photon photodissociation process. Under thermalized conditions, the OH fluorescence signal decreased with a half life of approximately 100 μsec with respect to the pump/probe delay in 0.7 Torr nitrogen buffer gas. This is comparable with the expected diffusion time out of the photolysis zone.

The OH(v=0) rotational distributions were taken from (1,0) R<sub>1</sub> and R<sub>2</sub> branch intensities. The intensities were converted to rotational populations using fluorescence excitation line strength factors calculated by the formulas of Greene and Zare.<sup>40</sup> It was assumed that the OH photofragments had an isotropic M<sub>J</sub> distribution. The nascent distributions, which are plotted in Figure 1, were found to be somewhat hotter than for thermalized samples. The distributions are essentially identical for all three oxime precursors and exhibit a preference for production of the F<sub>1</sub>(Ω = 3/2) over the F<sub>2</sub>(Ω = 1/2) spin-orbit component, particularly at low N.

The OH(v=1)/OH(v=0) population ratio was also estimated for acetaldoxime precursor since high-N P<sub>1</sub> and P<sub>2</sub> lines of the (1,0) band overlapped the (2,1) band origin, as shown in Figure 2. We estimate that the nascent v = 1 to v = 0 ratio equals 0.02 ± 0.01. In deriving this ratio, a correction for predissociation<sup>41,42</sup> of the low N levels of v'=2 was made. From the measured OH internal state distribution, we conclude that an average of only 2.5 kcal/mole appears as excitation of the OH fragments for acetaldoxime precursor. Similar results apply to formaldoxime and acetoxime. Thus, the overwhelming

majority of the energy available to the fragments must be present as translational recoil and internal excitation of the  $R_1R_2CN$  fragment.

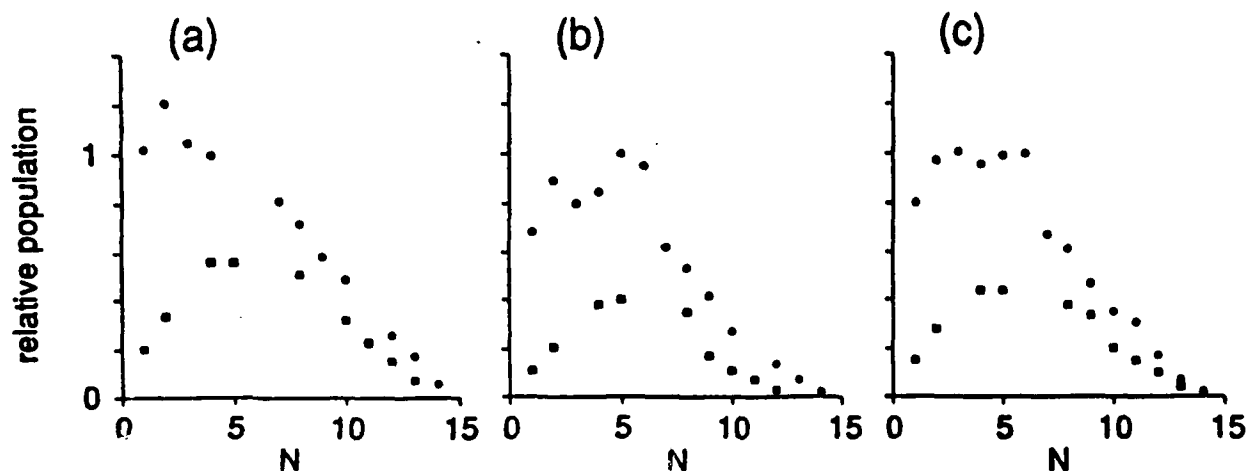


Figure 1. Rotational State Populations for OH ( $v=0$ ) Produced in the 193-nm Photodissociation of (a) Formaldoxime, (b) Acetaldoxime, and (c) Acetoxime. The circles and squares represent the  $F_1(\Omega=3/2)$  and  $F_2(\Omega=1/2)$  spin-orbit levels, respectively. The distributions are each separately normalized to a particular  $F_1$  level. The populations are not divided by the  $(2J+1)$  degeneracy factor.

### C. Search for $H_2CN$ Fluorescence

With OH detected as a photofragment from the oximes, it can be assumed that  $H_2CN$ , or its homologs, will be present in the photolysis at the same concentration as OH if no subsequent excimer-laser-induced decomposition or reactions of  $R_1R_2CN$  occur. (In Section D, we address the possibility that this assumption may not be correct.) Extensive searches for laser fluorescence signals from  $H_2CN$  and its homologs were carried out, both under nascent and thermalized conditions. No fluorescence signals attributable to these species could be found. For the formaldoxime precursor, scans were taken over 280–286 nm in the region of the strongest absorption bands seen in the flash photolysis experiments on formaldoxime<sup>10,11,13</sup> and formaldazine.<sup>12</sup> Because of the ease of introducing the precursor into the apparatus, the photolysis of acetaldoxime and acetoxime were more extensively studied. For these molecules, scans were taken over the range 287–295 nm in the regions where  $CH_3CHN$  and  $(CH_3)_2CN$  have been found to absorb.<sup>12</sup>

From our lack of observation of  $R_1R_2CN$  fluorescence and our observed signal-to-noise ratio for OH lines, we can estimate an upper limit to the  $R_1R_2CN$  fluorescence quantum yield, provided we assume that the concentrations of  $R_1R_2CN$  and OH are equal in the photolysis zone. Ogilvie and Horne<sup>10</sup> have estimated the integrated oscillator strength for the 280 nm band of  $H_2CN$  to be  $(4 \pm 2) \times 10^{-4}$ . We shall assume that the oscillator strength of the

corresponding bands in the radicals produced from acetaldoxime and acetoxime are similar. Since the band is approximately  $200 \text{ cm}^{-1}$  wide, this implies an average oscillator strength per unit bandwidth of  $2 \times 10^{-6}/\text{cm}^{-1}$ . We can estimate the oscillator strengths of the OH (1,0) and (2,1) bands from the known radiative lifetimes and fluorescence branching ratios:<sup>43-46</sup>  $f_{1,0} = 3.1 \times 10^{-4}$  and  $f_{2,1} = 4.5 \times 10^{-4}$ .

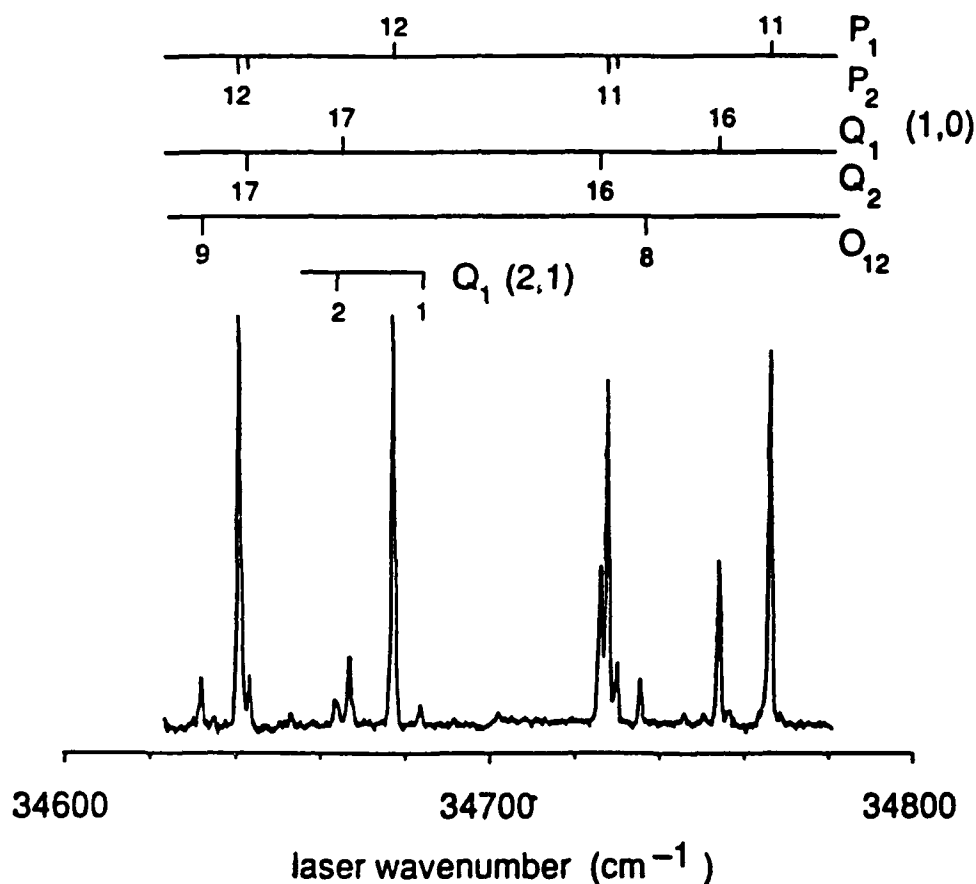


Figure 2. Excitation Spectrum Near the OH A-X (2,1) Band Origin for Photodissociation of Acetaldoxime Under Nascent Conditions. Lines of the (1,0) band and of the (2,1)  $O_1$  branch are marked. The pressure and pump/probe delay were 4 mTorr and 3  $\mu\text{s}$ , respectively.

Our most sensitive searches for  $R_1R_2\text{CN}$  fluorescence were carried out with acetaldoxime and acetoxime and with nitrogen added as a thermalizing buffer. Under these conditions, lines in the OH (2,1) band could be observed with signal-to-noise ratio of greater than 100 in some scans. The oscillator strengths given in the previous paragraph and the previously determined OH ( $v=1$ ) to ( $v=0$ ) population ratio imply that the ratio of an  $R_1R_2\text{CN}$  signal to that of a low N line in the OH (2,1) band should equal approximately unity if the fluorescence quantum yield  $\phi$  of  $R_1R_2\text{CN}$  were unity, assuming also that the

quantum yield for OH excited fluorescence is also unity. This suggests that  $\phi$  is less than 1% for  $\text{CH}_3\text{CHCN}$  and  $(\text{CH}_3)_2\text{CN}$ .

The  $\text{N}_2$  pressure and delay time of these scans were sufficiently low to prevent vibrational relaxation<sup>47</sup> in the  $\text{OH}(X^2\Pi)$  state. In fact, the zero-pressure fluorescence quantum yield for  $\text{OH } v'=2$  is considerably less than unity because of predissociation.<sup>41,42</sup> The measured radiative lifetime (ca. 450 nsec, which is significantly longer than the lifetime of low N levels in  $v'=2$  under collision-free conditions<sup>41,42</sup>) of the laser excited  $\text{OH}(v'=2)$  indicated that vibrational relaxation<sup>48</sup> to the nonpredissociating lower vibrational levels was occurring in the  $A^2\Sigma^+$  state; this would have the effect of substantially raising the fluorescence quantum yield over that for  $v'=2$  in the absence of collisions.<sup>41,42</sup> Our estimate for the upper bound on  $\phi$  would be even further reduced if the quantum yield of OH fluorescence were less than unity. Hence, we conclude  $\phi$  is certainly less than 1% for  $\text{CH}_3\text{CHCN}$  and  $(\text{CH}_3)_2\text{CN}$ . The derived upper limit for  $\phi$  is approximately one order of magnitude larger for  $\text{H}_2\text{CN}$  since the OH signals observed for formaldoxime precursor were smaller.

While not observing fluorescence attributable to  $\text{R}_1\text{R}_2\text{CN}$ , we did observe weak fluorescence from an as yet unidentifiable species other than OH. Figure 3 shows an excitation spectrum of a thermalized sample of photolyzed acetaldoxime in the region of the OH (2,1) band head. In contrast to the nascent spectrum in Figure 2, the high N lines of the OH (1,0) band are very weak compared to those of the (2,1) band because of rotational relaxation in  $v''=1$ . In addition to the strong OH lines, we can see a weak set of lines with closer spacing which appear to be converging to a band head degraded to the red near  $34650 \text{ cm}^{-1}$ . In addition to these lines, a second set of more closely spaced lines were observed around  $34150 \text{ cm}^{-1}$ , as shown in Figure 4. The spacing between lines in the latter region is much smaller than in the former.

We do not believe that these lines are due to  $\text{R}_1\text{R}_2\text{CN}$  since (1) they do not match the wavelengths reported for  $\text{R}_1\text{R}_2\text{CN}$  from the flash photolysis studies and, more importantly, (2) they appear at identical wavelengths with acetoxime as the precursor. (The lines near  $34650 \text{ cm}^{-1}$  also appeared, weakly, with formaldoxime.) In an attempt to identify the molecular carrier of these lines, we measured the radiative lifetimes of several of the lines. We estimate the fluorescence decay lifetime to be approximately  $1 \mu\text{sec}$ , roughly independent of the line excited and the nitrogen pressure over 0.3-1 Torr. The precision of our measurement is poor because the signal is small compared with the probe laser scattered light. One possible candidate for the molecular species is methoxy,  $\text{CH}_3\text{O}$ , which does have bands in this region<sup>49</sup> and whose radiative lifetime is reported to be  $1.5 \mu\text{sec}$ .<sup>50</sup> However, the rotational structure for a room-temperature sample of methoxy would be expected to be much more dense than the spectra shown in Figures 3 and 4.

At present, we do not have a suitable candidate species to attribute to these bands. We do, however, have several comments to make about the bands. Firstly, there is so much interference from the strong OH lines obscuring the short wavelength, better resolved band that it is difficult even to attempt to fit the rotational structure of the band. The OH lines make it particularly difficult to observe the band origin which would facilitate fitting the spectrum. Secondly, the splitting between the two bands is about  $450 \text{ cm}^{-1}$ .

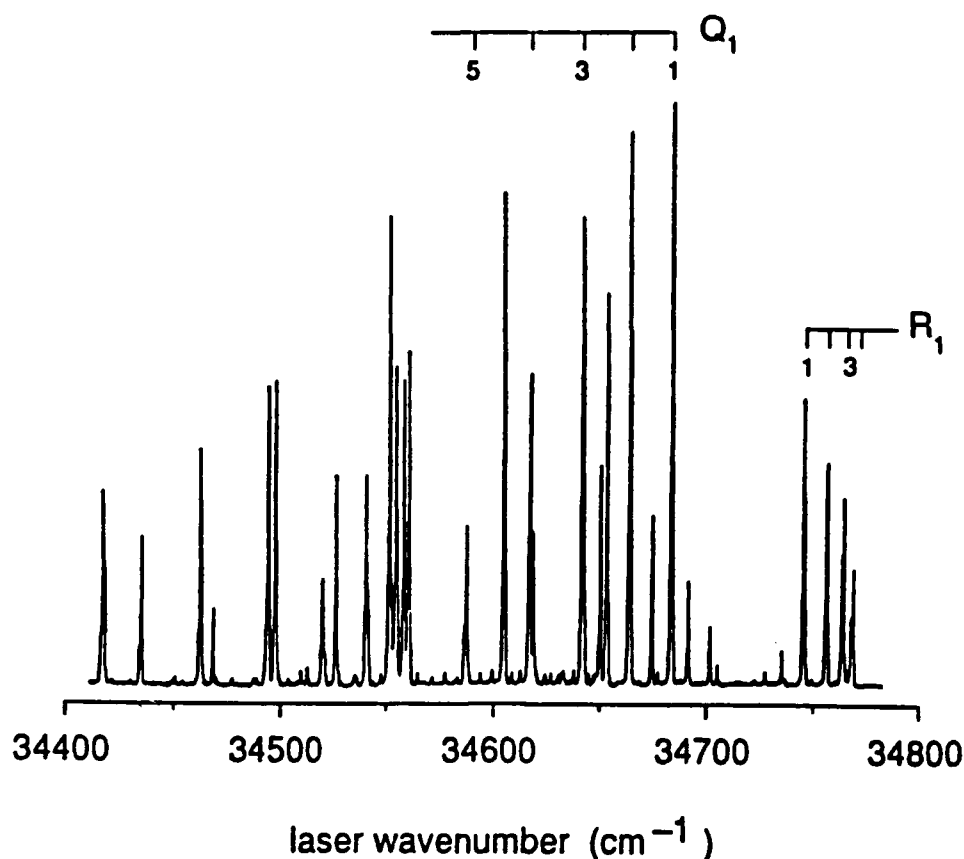


Figure 3. Excitation Spectrum Near the OH A-X (2,1) Band Origin for Photodissociation of Acetaldoxime Under Thermalized Conditions. All the strong lines are due to OH. The  $Q_1$  and  $R_1$  branches of the (2,1) band are marked. The splitting of the  $R_1$  branch lines is due to strong satellite transitions near the main branch lines for these low  $N$  values. The pressure and pump-probe delay were 0.66 Torr (nitrogen added) and 25  $\mu$ s, respectively.

This mitigates against the possibility that the two bands are subbands of the same vibrational band resulting from spin-orbit splitting because the splitting is so large. If the two bands belong to the same molecule, it would therefore seem that they are different vibrational bands. The form of the short wavelength bands appears to be much simpler than the long wavelength band. The former may consist of only P and R branches, with no apparent spin splitting, while the latter apparently has more branches. If the bands arise from the same molecular species, it therefore seems likely that the vibrational symmetries of the levels involved in the two bands are different. Alternatively, there could be a  $K'$  dependent predissociation in the short wavelength band, as in the  $\text{HCO } \tilde{A}^2A'' - \tilde{X}^2A'$  spectrum.<sup>20,21</sup>

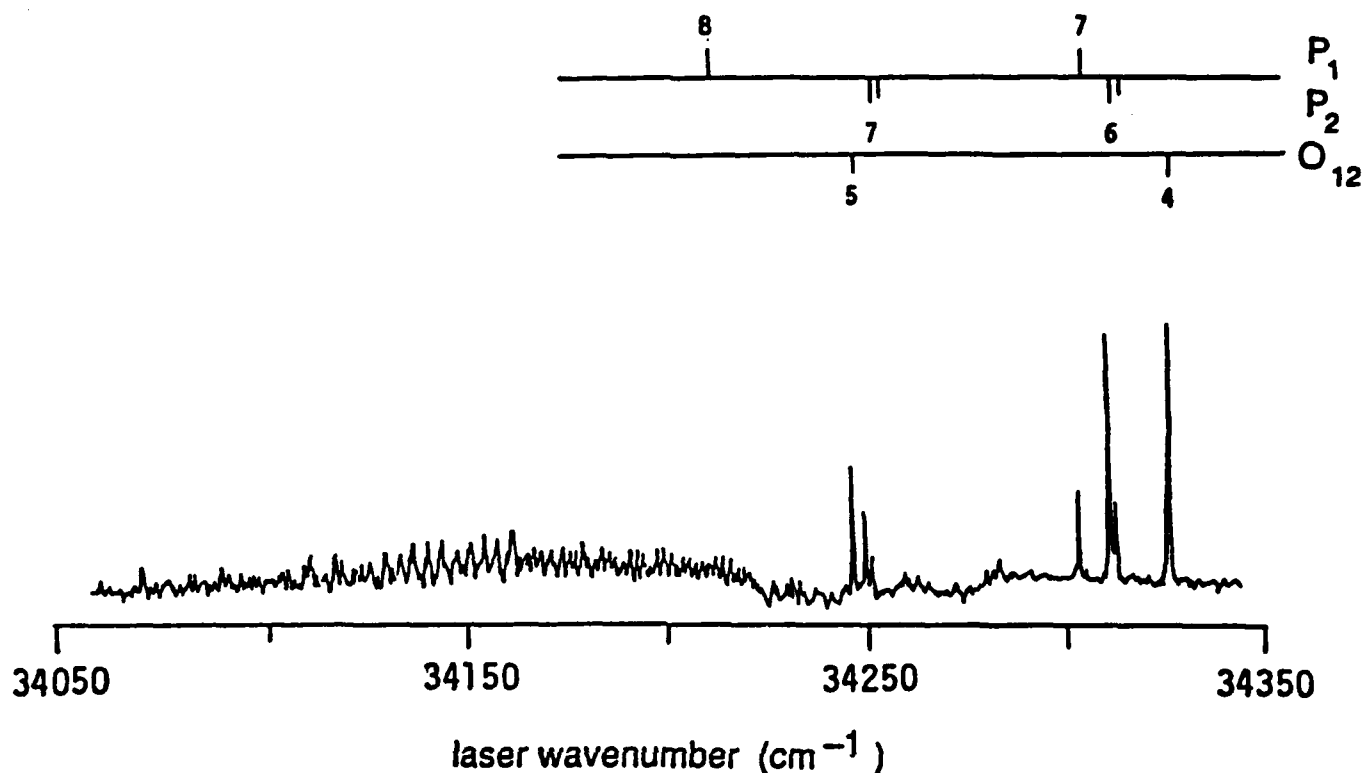


Figure 4. Excitation Spectrum Around 34150  $\text{cm}^{-1}$  for Photodissociation of Acetaldoxime Under Thermalized Conditions, Showing a Band of an Unidentified Species. Lines of the OH A-X (2,1) band are marked.

We also investigated the 193 nm photolysis of formaldazine and the 193 and 248 nm photolysis of acetaldazine. No fluorescence signals attributable to any molecular species were observed with the probe laser tuned through the wavelength regions where the appropriate  $R_1R_2\text{CN}$  fragments are known to absorb.<sup>10-13</sup> The sensitivity of these runs was less than those with oxime precursors. Moreover, our detection sensitivity could not be calibrated in situ since, of course, no OH is produced by the photolysis of these compounds.

#### D. Detection of CN

In estimating the upper bound to  $\phi$ , it is possible that our assumption of equal concentrations of the OH and  $R_1R_2\text{CN}$  photofragments may not be correct. The flash photolysis work<sup>10-13</sup> suggests that the latter is not rapidly consumed by chemical reactions since the  $R_1R_2\text{CN}$  absorptions were seen to persist at much higher reactant pressures than used in the present work for at least 80  $\mu\text{sec}$ . However, in our experiments, it is possible, at least in .



principle, that  $R_1R_2CN$  could itself be destroyed in the initial photodissociation since the energy available to the fragments considerably exceeds the  $R_1-R_2CN$  bond energy (see Section A) and only a small fraction of this energy appears as OH excitation (see Section B). Thus, both  $R_1R_2CN + OH$  and  $R_1CN + R_2 + OH$  photolysis products could be formed in a one-photon process. The dissociation wavelength in the present experiment (193 nm) is somewhat shorter than in the flash photolysis studies since the Kr flashlamp output there dropped rapidly below 200 nm.<sup>12</sup> The effective wavelength range of the photolysis radiation is actually a convolution of the flashlamp output and the oxime absorption coefficient, which is rapidly rising below 200 nm. Hence, it is possible that fragmentation of  $R_1R_2CN$  is more likely with photolysis using 193 nm radiation, than with a Kr flashlamp. In fact, the appearance of successive absorption maxima in the continuum spectra of both the oxime and azine precursors<sup>10,12,13</sup> as one goes toward shorter wavelengths may indicate the onset of some fraction of higher fragmentation photolysis.

In an effort to determine the importance of such destruction of  $R_1R_2CN$ , we looked for production of CN by laser fluorescence excitation. Indeed, we observed CN through fluorescence excitation in its  $B^2\Sigma^+ - X^2\Sigma^+ (0,0)$  band upon 193 nm photolysis of acetaldoxime. No attempt was made to measure quantitatively the CN concentration relative to that of OH because of the widely different wavelength range, and laser and filter bandwidths. However, we estimate that the CN concentration was significantly less than that of OH since comparable photomultiplier signals were observed; the oscillator strength of the CN B-X (0,0) band equals  $(3.11 \pm 0.05) \times 10^{-2}$ <sup>51</sup> and is hence much larger than for the OH ( $\Delta v=+1$ ) sequence. The dependence of the CN fluorescence signal was investigated for several lines as a function of excimer laser pulse energy under thermalizing conditions (1.0 Torr nitrogen added, 4  $\mu$ sec pump/probe delay). On a log-log plot, the slope was found to equal  $0.78 \pm 0.1$ . This suggests that CN is formed by a one-photon dissociation process from the oxime. The process  $CH_3CHNOH \rightarrow CH_4 + CN + OH$  requires approximately 110 kcal/mole. This dissociation pathway is clearly feasible in a one-photon process at 193 nm.

In addition to the observation of ground state CN by laser fluorescence detection, an emission signal coincident with the ArF excimer laser pulse was seen through the 390 nm bandpass filter with the acetaldoxime precursor. We do not believe this is due to direct photolytic production of  $CN(B^2\Sigma^+)$  because the decay time of this signal (ca. 1  $\mu$ sec) is much longer than the  $CN(B)$  radiative lifetime (ca. 70 nsec<sup>51</sup>). The dependence of the emission signal on the excimer pulse energy was found to be approximately linear (slope of  $0.99 \pm 0.1$  on a log-log plot). However, production of  $CN(B)$  in a one-photon process at 193 nm is not energetically allowed. Unfortunately, it was not possible in the present apparatus to take a spectrum of this emission; thus elucidating the species responsible.

#### IV. CONCLUSION

In this work, we have investigated the 193 nm photodissociation of the simplest oximes, namely formaldoxime, acetaldoxime, and acetoxime. The OH photofragment was detected, and its internal state distribution determined. An unsuccessful search was made to observe laser excited fluorescence from the other photofragment  $R_1R_2CN$ , where  $R_1$  and  $R_2$  equals H or  $CH_3$ . Based on the assumption of an equal concentration of OH and  $R_1R_2CN$  upon photolysis of the

oxime, we were able to estimate a rough upper bound of 1% for the fluorescence quantum yield  $\phi$  of the  $R_1R_2CN$  absorption bands in the 280-295 nm region. This implies that electronic states excited in these transitions are predissociative. Through the detection of CN, there is some evidence that the  $R_1R_2CN$  is itself destroyed to some extent in the initial event of the 193 nm photodissociation of the oxime. This could have the effect of increasing our estimate on the upper bound to  $\phi$ .

The present study indicates that fluorescence excitation of the electronic bands near 280 nm of methyleneamidogen is not a feasible laser diagnostic for this species. The infrared absorption bands of  $H_2CN$ , which have been identified in the recent matrix study of Jacox,<sup>14</sup> may have utility as a probe for this molecule. An alternative, more sensitive technique may be resonant-enhanced multiphoton ionization through a Rydberg state, as has been successfully carried out for HCO.<sup>24,25</sup>

Recently, Marston, et al.,<sup>52</sup> have shown that  $H_2CN$  can be produced in high yield from the  $N + CH_3$  reaction. Using the discharge flow/mass spectrometry technique, this group has measured the elementary reaction rate constant for the  $N + H_2CN$  reaction. These results imply that mass spectrometric detection of  $H_2CN$  may be a viable alternative diagnostic for this species. In addition, it would be interesting to compare the production of  $H_2CN$  by this chemical method with our photolytic approach.

#### ACKNOWLEDGMENT

We appreciate the assistance of M.A. Schroeder in the synthesis of several of the precursors. We also acknowledge M.A. Schroeder, R.A. Pifer, and K.L. McNesby for their aid in identification of these precursors. We thank B.J. Gaffney for the loan of a distillation apparatus used in the syntheses. P.J.D. acknowledges the support of the U.S. Army Research Office under contract number DAAL-03-88-K-0031 and the National Science Foundation under grant number CHE-8700970. A.W.M. acknowledges partial support from the Air Force Office of Scientific Research, Directorate of Aerospace Sciences, under contract number 89-0017.

INTENTIONALLY LEFT BLANK.

## REFERENCES

1. D.R. Crosley, Ed., "Laser Probes for Combustion Chemistry", Amer. Chem. Soc. Symposium Series; Amer. Chem. Soc., Washington, DC, Vol. 134, 1980.
2. J.H. Bechtel, C.J. Dasch, R. Teets, In Laser Applications, J.F. Ready and R.K. Erf, Eds.; Academic Press, New York, Vol. 5, p 129, 1983.
3. (a) D.R. Crosley, "Collisional Effects on Laser-Induced Fluorescence Flame Measurements", Opt. Eng., Vol. 20, p. 511, 1981; (b) D.R. Crosley and G.P. Smith, "Laser-Induced Fluorescence Spectroscopy for Combustion Diagnostics", Opt. Eng., Vol. 22, p. 545, 1983.
4. E.L. Cochran, F.J. Adrian, and V.A. Bowers, "ESR Detection of the Cyanogen and Methylene Imino Free Radicals", J. Chem. Phys., Vol. 36, p. 1938, 1962.
5. D. Banks and W. Gordy, "Electron Spin Resonance and Bond Structure of  $H_2CN$ ", Mol. Phys., Vol. 26, p. 1555, 1973.
6. D. Behar and R.W. Fessenden, "An Electron Spin Resonance Investigation of the Reactions in Irradiated Aqueous Solutions of Hydrogen Cyanide and the Cyanide Ion", J. Phys. Chem., Vol. 76, p. 3945, 1972.
7. M. Fujiwara, N. Tamura, and H. Hirai, "Electron Spin Resonance Study on Photoinduced Changes of the Radicals Produced in Methyl Isocyanate Solid Irradiated with Gamma Rays", Bull. Chem. Soc. Japan, Vol. 46, p. 701, 1973.
8. M.C.R. Symons, "The Importance of Imino Radicals ( $R_2C=N$ ) as Reaction Intermediates", Tetrahedron, Vol. 29, p. 615, 1973.
9. C.U. Morgan and R.A. Beyer, "Electron-Spin-Resonance Studies of HMX Pyrolysis Products", Combust. Flame, Vol. 36, p.99, 1979.
10. J.F. Ogilvie and D.G. Horne, "Electronic Absorption Spectra of Methanal Azine and the Methyleniminyl Free Radical", J. Chem. Phys., Vol. 48, p. 2248, 1968.
11. J.F. Ogilvie, "Assignments of Electronic Transitions in Methanal Azine and Related Molecules", Can. J. Spectrosc., Vol. 19, p. 89, 1974.
12. D.G. Horne and R.G.W. Norrish, "The Photolysis of Acyclic Azines and the Electronic Spectra of  $R_1R_2CN_7$  Radicals", Proc. R. Soc. London A, Vol. 315, p. 301, 1970.
13. D.G. Horne and R.G.W. Norrish, "The Flash Photolysis of Oximes", Proc. R. Soc. London A, Vol. 315, p. 287, 1970.
14. M.E. Jacox, "Vibrational and Electronic Spectra of the  $H + HCN$  Reaction Products Trapped in Solid Argon", J. Phys. Chem., Vol. 91, p. 6595, 1987.

15. R.A. Fifer, "Chemistry of Nitrate Ester and Nitramine Propellants", In *Fundamentals of Solid-Propellant Combustion*; K.K. Kuo and M. Summerfield, Eds., Prog. in Aeronautics and Astronautics, Vol. 90, p. 177, 1984.
16. C.F. Melius and J.S. Binkley, "Thermochemistry of the Decomposition of Nitramines in the Gas Phase", *Proceedings of the 21st International Symposium on Combustion*, Combustion Institute, Pittsburgh, PA, p. 1953, 1986.
17. X. Zhao, E. Hintsa, and Y.T. Lee, "Infrared Multiphoton Decomposition of RDX in a Molecular Beam", *J. Chem. Phys.*, Vol. 88, p. 801, 1988.
18. R.A. Bair and T.H. Dunning, Jr. "Theoretical Studies of the Reactions of HCN with Atomic Hydrogen", *J. Chem. Phys.*, Vol. 82, p. 2280, 1985.
19. G.F. Adams, D.R. Yarkony, R.J. Bartlett, and G.D. Purvis, "Electronic Structure and Vertical Excitation Spectrum of Methyleneamidogen  $\text{CH}_2\text{N}$ ", *Intl. J. Quantum Chem.*, Vol. 23, p. 437, 1983.
20. J.W.C. Johns, S.H. Priddle, and D.A. Ramsay, "Electronic Absorption Spectrum of HCO and DCO Radicals", *Discuss. Faraday Soc.*, Vol. 35, p. 90, 1963.
21. R. Vasudev and R.N. Zare, "Laser Optogalvanic Study of HCO  $\tilde{\text{A}}$  State Predissociation", *J. Chem. Phys.*, Vol. 76, p. 5267, 1982.
22. R. Konig and J. Lademann, "Laser-Induced Fluorescence Detection of HCO Produced by Laser Photolysis of Formaldehyde", *Chem. Phys. Lett.*, Vol. 94, p. 152, 1983.
23. B.M. Stone, M. Noble, and E.K.C. Lee, "Laser-Induced Fluorescence Emission from HCO Produced by 308 nm Excimer Laser Photodissociation of Acetaldehyde", *Chem. Phys. Lett.*, Vol. 118, p. 83, 1985.
24. P.J.H. Tjossem, P.M. Goodwin, and T.A. Cool, "Two-Photon Resonance REMPI Detection of the Formyl Radical", *J. Chem. Phys.*, Vol. 84, p. 5334, 1986.
25. J.S. Bernstein, X.M. Song, and T.A. Cool, "Detection of the Formyl Radical in a Methane/Oxygen Flame by Resonance Ionization", *Chem. Phys. Lett.*, Vol. 145, p. 188, 1988.
26. R. Scholl, "Das Einfachste Normale Oxim  $\text{H}_2\text{C:NOH}$  und Sein Polymeres", *Berichte*, Vol. 24, p. 573, 1891.
27. P.J. Dagdigian, "State Resolved Cross Sections for Rotationally Inelastic Collisions of  $\text{NH}_2(\tilde{\text{A}}\text{B}_1)$  with Helium", *J. Chem. Phys.*, Vol. 90, p. 2617, 1989.
28. Th. Curtius and E. Zinkeisen, "Die Umlagerung von Ketazinen und Aldazinen der Fettreihe in Pyrazolinderivate", *J. Prakt. Chem.*, Vol. 58, p. 325, 1898.

29. V. Tabacik and V. Pellegrin, "Vibrations Fondamentales des Espèces d0, d2, et d6 Totalement Symétriques de L'acétaldazine Anti-anti", Spectrochim. Acta, Vol. 35A, p. 961, 1979.
30. B. Zeeh and R. Beutler, "Elektronenstoss-Induzierte Meleküllagerungen. I. Massenspektrometrische Fragmentierungen von Azinen und Phosphazinen", Organic Mass Spectrom., Vol. 1, p. 791, 1968.
31. G. Pulvermacher, "Zur Kenntniss des Formaldehyds", Berichte, Vol. 26, p. 2360, 1893.
32. K.A. Hofmann and D. Storm, "Tetraformal-trisazin aus Formaldehyd und Hydrazinhydrat, ein Neues Reduktionsmittel für Analytische Chemie", Berichte, Vol. 45, p. 1725, 1912.
33. N.P. Neureiter, "Monomeric Formaldazine-Synthesis of 1,3,4-Thiadiazolidine - A New Heterocycle", J. Am. Chem. Soc., Vol. 81, p. 2910, 1959.
34. J.F. Ogilvie and K.C. Cole, "Vibrational Spectra and Conformation of Methanal Azine", Spectrochim. Acta, Vol. 27A, p. 877, 1971. See also J.F. Ogilvie, S.J. Cyvin, and B.N. Cyvin, "Harmonic Force Fields and Mean Amplitudes of Vibration for Some Molecules Containing Nitrogen: Methanal Azine", J. Molec. Structure, Vol. 18, p. 285, 1973.
35. V.E. Bondybey and J.W. Nibler, "Infrared and Raman Spectra of Formaldazine", Spectrochim. Acta, Vol. 29A, p. 645, 1973.
36. S. Califano and W. Luttke, "Infrarotuntersuchungen an Oximen. II. Die Schwingungsspektren des Formaldoxims und des Acetonoxims", Z. Physik. Chem., Neue Folge, Vol. 6, p. 83, 1956.
37. S.W. Benson and H.E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", Natl. Stand. Ref. Data Ser., U.S., Natl. Bur. Stand., p. 21, 1970.
38. M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr.; D.J. Frurip, R.A. McDonald, and A.N. Syverud, "JANAF Thermochemical Tables, 3rd Edition", J. Phys. Chem. Ref. Data, Vol. 14, Supplement 1, 1985.
39. M. McKee and C.F. Melius, Private communication.
40. C.H. Greene and R.N. Zare, "Determination of Product Population and Alignment Using Laser-Induced Fluorescence", J. Chem. Phys., Vol. 78, p. 6741, 1983.
41. K.R. German, "Radiative and Predissociative Lifetimes of the  $v' = 0, 1$ , and 2 Levels of the  $A^2\Sigma^+$  State of OH and OD", J. Chem. Phys., Vol. 63, p. 5252, 1975.
42. J. Brzozowski, P. Erman, and M. Lyyra, "Precision Estimates of the Predissociation Rates of the OH  $A^2\Sigma$  State ( $v' < 2$ )", Phys. Scripta, Vol. 17, p. 507, 1978.

43. W.L. Dimpfl and J.L. Kinsey, "Radiative Lifetimes of OH ( $A^2\Sigma$ ) and Einstein Coefficients for the A-X System of OH and OD", J. Quant. Spectrosc. Radiat. Transfer, Vol. 21, p. 233, 1979.
44. I.S. McDermid and J.B. Laudenslager, "Radiative Lifetimes and Quenching Rate Coefficients for Directly Excited Rotational Levels of OH ( $A^2\Sigma^+ v'=0$ )", J. Chem. Phys., Vol. 76, p. 1824, 1982.
45. D.R. Crosley and R.K. Lengel, "Relative Transition Probabilities in the A-X System of OD", J. Quant. Spectrosc. Radiat. Transfer, Vol. 17, p. 59, 1977.
46. R.A. Copeland, J.B. Jeffries, and D.R. Crosley, "Transition Probabilities in OH  $A^2\Sigma^+ - X^2\Pi$ : Bands with  $v'=0$  and 1,  $v''=0$  to 4", Chem. Phys. Lett., Vol. 138, p. 425, 1987.
47. K.J. Rensberger, J.B. Jeffries, and D.R. Crosley, "Vibrational Relaxation in OH ( $X^2\Pi$ ,  $v=2$ )", J. Chem. Phys., Vol. 90, p. 2174, 1989.
48. R.A. Copeland, M.L. Wise, and D.R. Crosley, "Vibrational Energy Transfer and Quenching of OH ( $A^2\Sigma^+$ ,  $v'=1$ )", J. Phys. Chem., Vol. 92, p. 5710, 1988.
49. S.C. Foster, P. Misra, T.Y.D. Lin, C.P. Damo, C.C. Carter, and T.A. Miller, "Free Jet Cooled Laser-Induced Fluorescence Spectrum of Methoxy. 1. Vibronic Analysis of the  $\tilde{A}$  and  $\tilde{X}$  States", J. Phys. Chem., Vol. 92, p. 5914, 1988.
50. G. Inoue, J. Akimoto, and M. Okuda, "Laser-Induced Fluorescence Spectra of  $CH_3O$ ", Chem. Phys. Lett., Vol. 63, p. 213, 1979.
51. N. Duric, P. Erman, and M. Larsson, "The Influence of Collisional Transfers and Perturbations on Measured A and B State Lifetimes in CN", Phys. Scripta, Vol. 18, p. 39, 1978.
52. G. Marston, F.L. Nesbitt, and L.J. Stief, "Branching Ratios in of N Atoms with N +  $CH_3$  Reaction: Formation of the Methyleneamidogen ( $H_2CN$ ) Radical", J. Chem. Phys., Vol. 91, p. 3483, 1989.



No of Copies	Organization	No of Copies	Organization
1	Office of the Secretary of Defense OUSD(A) Director, Live Fire Testing ATTN: James F. O'Bryon Washington, DC 20301-3110	1	Director US Army Aviation Research and Technology Activity Ames Research Center Moffett Field, CA 94035-1099
2	Administrator Defense Technical Info Center ATTN: DTIC-DDA Cameron Station Alexandria, VA 22304-6145	1	Commander US Army Missile Command ATTN: AMSMI-RD-CS-R (DOC) Redstone Arsenal, AL 35898-5010
1	HQDA (SARD-TR) WASH DC 20310-0001	1	Commander US Army Tank-Automotive Command ATTN: AMSTA-TSL (Technical Library) Warren, MI 48397-5000
1	Commander US Army Materiel Command ATTN: AMCDRA-ST 5001 Eisenhower Avenue Alexandria, VA 22333-0001	1	Director US Army TRADOC Analysis Command ATTN: ATAA-SL White Sands Missile Range, NM 88002-5502
1	Commander US Army Laboratory Command ATTN: AMSLC-DL Adelphi, MD 20783-1145	(Class. only) 1	Commandant US Army Infantry School ATTN: ATSH-CD (Security Mgr.) Fort Benning, GA 31905-5660
2	Commander US Army, ARDEC ATTN: SMCAR-IMI-I Picatinny Arsenal, NJ 07806-5000	(Unclass. only) 1	Commandant US Army Infantry School ATTN: ATSH-CD-CSO-OR Fort Benning, GA 31905-5660
2	Commander US Army, ARDEC ATTN: SMCAR-TDC Picatinny Arsenal, NJ 07806-5000	1	Air Force Armament Laboratory ATTN: AFATL/DLODL Eglin AFB, FL 32542-5000
1	Director Benet Weapons Laboratory US Army, ARDEC ATTN: SMCAR-CCB-TL Watervliet, NY 12189-4050		<u>Aberdeen Proving Ground</u>
1	Commander US Army Armament, Munitions and Chemical Command ATTN: SMCAR-ESP-L Rock Island, IL 61299-5000	2	Dir, USAMSAA ATTN: AMXSY-D AMXSY-MP, H. Cohen
1	Commander US Army Aviation Systems Command ATTN: AMSAV-DACL 4300 Goodfellow Blvd. St. Louis, MO 63120-1798	1	Cdr, USATECOM ATTN: AMSTE-TD
		3	Cdr, CRDEC, AMCCOM ATTN: SMCCR-RSP-A SMCCR-MU SMCCR-MSI
		1	Dir, VLAMO ATTN: AMSLC-VL-D

<u>No. of Copies</u>	<u>Organization</u>	<u>No. of Copies</u>	<u>Organization</u>
4	Commander US Army Research Office ATTN: R. Ghirardelli D. Mann R. Singleton R. Shaw P.O. Box 12211 Research Triangle Park, NC 27709-2211	1	Commander Naval Surface Warfare Center ATTN: J. L. East, Jr., G-23 Dahlgren, VA 22448-5000
2	Commander Armament RD&E Center US Army AMCCOM ATTN: SMCAR-AEE-B, D. S. Downs SMCAR-AEE, J. A. Lannon Picatinny Arsenal, NJ 07806-5000	2	Commander Naval Surface Warfare ATTN: R. Bernecker, R-13 G. B. Wilmot, R-16 Silver Spring, MD 20902-5000
1	Commander Armament RD&E Center US Army AMCCOM ATTN: SMCAR-AEE-BR, L. Harris Picatinny Arsenal, NJ 07806-5000	5	Commander Naval Research Laboratory ATTN: M. C. Lin J. McDonald E. Oran J. Shnur R. J. Doyle, Code 6110 Washington, DC 20375
2	Commander US Army Missile Command ATTN: AMSMI-RK, D. J. Ifshin W. Wharton Redstone Arsenal, AL 35898	1	Commanding Officer Naval Underwater Systems Center Weapons Dept. ATTN: R. S. Lazar/Code 36301 Newport, RI 02840
1	Commander US Army Missile Command ATTN: AMSMI-RKA, A. R. Maykut Redstone Arsenal, AL 35898-5249	1	Commandant USAFAS ATTN: ATSF-TSM-CN Fort Sill, OK 73503-5600
1	Office of Naval Research Department of the Navy ATTN: R. S. Miller, Code 432 800 N. Quincy Street Arlington, VA 22217	1	Superintendent Naval Postgraduate School Dept. of Aeronautics ATTN: D. W. Netzer Monterey, CA 93940
1	Commander Naval Air Systems Command ATTN: J. Ramnarace, AIR-54111C Washington, DC 20360	4	AL/LSCF ATTN: R. Corley R. Geisler J. Levine D. Weaver Edwards AFB, CA 93523-5000
		1	AL/MKPB ATTN: B. Goshgarian Edwards AFB, CA 93523-5000
		1	AFOSR ATTN: J. M. Tishkoff Bolling Air Force Base Washington, DC 20332

<u>No. of Copies</u>	<u>Organization</u>
1	NASA Langley Research Center Langley Station ATTN: G. B. Northam/ MS 168 Hampton, VA 23365
4	National Bureau of Standards ATTN: J. Hastie M. Jacox T. Kashiwagi H. Senerjian US Department of Commerce Washington, DC 20234
1	OSD/SDIO/UST ATTN: L. H. Caveny Pentagon Washington, DC 20301-7100
1	Aerojet Solid Propulsion Co. ATTN: P. Micheli Saramento, CA 95813
1	Applied Combustion Technology, Inc. ATTN: A. M. Varney P.O. Box 17885 Orlando, FL 32860
2	Applied Mechanics Reviews The American Society of Mechanical Engineers ATTN: R. E. White A. B. Wenzel 345 E. 47th Street New York, NY 10017
1	Atlantic Research Corp. ATTN: M. K. King 5390 Cherokee Avenue Alexandria, VA 22314
1	Atlantic Research Corp. ATTN: R. H. W. Waesche 7511 Wellington Road Gainesville, VA 22065
1	AVCO Everett Rsch. Lab. Div. ATTN: D. Stuckler 2385 Revere Beach Parkway Everett, MA 02149

<u>No. of Copies</u>	<u>Organization</u>
1	Battelle Memorial Institute Tactical Technology Center ATTN: J. Huggins 505 King Avenue Columbus, OH 43201
1	Cohen Professional Services ATTN: N. S. Cohen 141 Channing Street Redlands, CA 92373
1	Exxon Research and Eng. Co. ATTN: A. Dean Route 22E Annandale, NJ 08801
1	Ford Aerospace and Communications Corp. DIVAD Division Div. Hq., Irvine ATTN: D. Williams Main Street and Ford Road Newport Beach, CA 92663
1	General Applied Science Laboratories, Inc. 77 Raynor Avenue Ronkonkama, NY 11779-6649
1	General Electric Armament and Electrical Systems ATTN: M. J. Bulman Lakeside Avenue Burlington, VT 05401
1	General Electric Company 2352 Jade Lane Schenectady, NY 12309
1	General Electric Ordnance Systems ATTN: J. Mandzy 100 Plastics Avenue Pittsfield, MA 01203
2	General Motors Rach Labs Physics Department ATTN: T. Sloan R. Teets Warren, MI 48090

No. of Copies	Organization
2	Hercules, Inc. Allegheny Ballistics Lab. ATTN: William B. Walkup E. A. Yount P.O. Box 210 Rocket Center, WV 26726
1	Honeywell, Inc. Government and Aerospace Products ATTN: D. E. Broden/ MS MN50-2000 600 2nd Street NE Hopkins, MN 55343
1	Honeywell, Inc. ATTN: R. E. Tompkins MN38-3300 10400 Yellow Circle Drive Minnetonka, MN 55343
1	IBM Corporation ATTN: A. C. Tam Research Division 5600 Cottle Road San Jose, CA 95193
1	IIT Research Institute ATTN: R. F. Remaly 10 West 35th Street Chicago, IL 60616
2	Director Lawrence Livermore National Laboratory ATTN: C. Westbrook M. Costantino P.O. Box 808 Livermore, CA 94550
1	Lockheed Missiles and Space Co. ATTN: George Lo 3251 Hanover Street Dept. 52-35/B204/2 Palo Alto, CA 94304
1	Los Alamos National Lab ATTN: B. Nichols T7, MS-B284 Los Alamos, NM 87545
1	National Science Foundation ATTN: A. B. Harvey Washington, DC 20550

No. of Copies	Organization
1	Olin Corporation Smokeless Powder Operations ATTN: V. McDonald P.O. Box 222 St. Marks, FL 32355
1	Paul Gough Associates, Inc. ATTN: P. S. Gough 1048 South Street Portsmouth, NH 03801-5423
2	Princeton Combustion Research Laboratories, Inc. ATTN: M. Summerfield N. A. Messina 475 US Highway One Monmouth Junction, NJ 08852
1	Hughes Aircraft Company ATTN: T. E. Ward 8433 Fallbrook Avenue Canoga Park, CA 91303
1	Rockwell International Corp. Rocketdyne Division ATTN: J. E. Flanagan/HB02 6633 Canoga Avenue Canoga Park, CA 91304
4	Sandia National Laboratories Combustion Sciences Dept. ATTN: R. Cattolica S. Johnston P. Mattern D. Stephenson Livermore, CA 94550
1	Science Applications, Inc. ATTN: R. B. Edelman 23146 Cumorah Crest Woodland Hills, CA 91364
3	SRI International ATTN: G. Smith D. Crosley D. Golden 333 Ravenswood Avenue Menlo Park, CA 94025
1	Stevens Institute of Tech. Davidson Laboratory ATTN: R. McAlevy, III Hoboken, NJ 07030

<u>No. of Copies</u>	<u>Organization</u>
1	Thiokol Corporation Elkton Division ATTN: S. F. Palopoli P.O. Box 241 Elkton, MD 21921
1	Thiokol Corporation Huntsville Division ATTN: R. Glick Huntsville, AL 35807
3	Thiokol Corporation Wasatch Division ATTN: S. J. Bennett P.O. Box 524 Brigham City, UT 84302
1	United Technologies ATTN: A. C. Eckbreth East Hartford, CT 06108
3	United Technologies Corporation Chemical Systems Division ATTN: R. S. Brown T. D. Myers (2 copies) P.O. Box 49028 San Jose, CA 95161-9028
1	Universal Propulsion Company ATTN: H. J. McSpadden Black Canyon Stage 1 Box 1140 Phoenix, AZ 85029
1	Veritay Technology, Inc. ATTN: E. B. Fisher 4845 Millersport Highway P.O. Box 305 East Amherst, NY 14051-0305
1	Brigham Young University Dept. of Chemical Engineering ATTN: M. W. Beckstead Provo, UT 84601
1	California Institute of Tech. Jet Propulsion Laboratory ATTN: MS 125/159 4800 Oak Grove Drive Pasadena, CA 91103

<u>No. of Copies</u>	<u>Organization</u>
1	California Institute of Technology ATTN: F. E. C. Culick/ MC 301-46 204 Karman Lab. Pasadena, CA 91125
1	University of California, Berkeley Mechanical Engineering Dept. ATTN: J. Daily Berkeley, CA 94720
1	University of California Los Alamos Scientific Lab. P.O. Box 1663, Mail Stop B216 Los Alamos, NM 87545
1	University of California, San Diego ATTN: F. A. Williams Dept. of Applied Mechanics and Engineering Sciences, B010 La Jolla, CA 92093
2	University of California, Santa Barbara Quantum Institute ATTN: K. Schofield M. Steinberg Santa Barbara, CA 93106
2	University of Southern California Dept. of Chemistry ATTN: S. Benson C. Wittig Los Angeles, CA 90007
1	Case Western Reserve Univ. Div. of Aerospace Sciences ATTN: J. Tien Cleveland, OH 44135
1	Cornell University Department of Chemistry ATTN: T. A. Cool Baker Laboratory Ithaca, NY 14853
1	Univ. of Dayton Rech Inst. ATTN: D. Campbell AL/PAP Edwards AFB, CA 93523

<u>No. of Copies</u>	<u>Organization</u>
1	University of Florida Dept. of Chemistry ATTN: J. Winefordner Gainesville, FL 32611
3	Georgia Institute of Technology School of Aerospace Engineering ATTN: E. Price W. C. Strahle B. T. Zinn Atlanta, GA 30332
1	University of Illinois Dept. of Mech. Eng. ATTN: H. Krier 144MEB, 1206 W. Green St. Urbana, IL 61801
1	Johns Hopkins University/APL Chemical Propulsion Information Agency ATTN: T. W. Christian Johns Hopkins Road Laurel, MD 20707
1	University of Michigan Gas Dynamics Lab Aerospace Engineering Bldg. ATTN: G. M. Faeth Ann Arbor, MI 48109-2140
1	University of Minnesota Dept. of Mechanical Engineering ATTN: E. Fletcher Minneapolis, MN 55455
3	Pennsylvania State University Applied Research Laboratory ATTN: K. K. Kuo H. Palmer M. Micci University Park, PA 16802
1	Pennsylvania State University Dept. of Mechanical Engineering ATTN: V. Yang University Park, PA 16802

<u>No. of Copies</u>	<u>Organization</u>
1	Polytechnic Institute of NY Graduate Center ATTN: S. Lederman Route 110 Farmingdale, NY 11735
2	Princeton University Forrestal Campus Library ATTN: K. Brezinsky I. Glassman P.O. Box 710 Princeton, NJ 08540
1	Purdue University School of Aeronautics and Astronautics ATTN: J. R. Osborn Grissom Hall West Lafayette, IN 47906
1	Purdue University Department of Chemistry ATTN: E. Grant West Lafayette, IN 47906
2	Purdue University School of Mechanical Engineering ATTN: N. M. Laurendeau S. N. B. Murthy TSPC Chaffee Hall West Lafayette, IN 47906
1	Rensselaer Polytechnic Inst. Dept. of Chemical Engineering ATTN: A. Fontijn Troy, NY 12181
1	Stanford University Dept. of Mechanical Engineering ATTN: R. Hanson Stanford, CA 94305
1	University of Texas Dept. of Chemistry ATTN: W. Gardiner Austin, TX 78712
1	University of Utah Dept. of Chemical Engineering ATTN: G. Flandro Salt Lake City, UT 84112

<u>No. of Copies</u>	<u>Organization</u>
1	Virginia Polytechnic Institute and State University ATTN: J. A. Schetz Blacksburg, VA 24061
1	F. J. Seiler Research Lab (AFSC) ATTN: S. A. Shackleford USAF Academy, CO 80840-6528
1	Freedman Associates ATTN: E. Freedman 2411 Diana Road Baltimore, MD 21209-1525

INTENTIONALLY LEFT BLANK.



## USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. BRL Report Number BRL-TR-3094 Date of Report May 1990

2. Date Report Received \_\_\_\_\_

3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

### CURRENT ADDRESS

\_\_\_\_\_  
Name

\_\_\_\_\_  
Organization

\_\_\_\_\_  
Address

\_\_\_\_\_  
City, State, Zip Code

### OLD ADDRESS

\_\_\_\_\_  
Name

\_\_\_\_\_  
Organization

\_\_\_\_\_  
Address

\_\_\_\_\_  
City, State, Zip Code

7. If indicating a Change of Address or Address Correction, please provide the New or Correct Address in Block 6 above and the Old or Incorrect address below.

(Remove this sheet, fold as indicated, staple or tape closed, and mail.)

-----FOLD HERE-----

**DEPARTMENT OF THE ARMY**

Director  
U.S. Army Ballistic Research Laboratory  
ATTN: SLCBR-DD-T  
Aberdeen Proving Ground, MD 21005-5066  
**OFFICIAL BUSINESS**

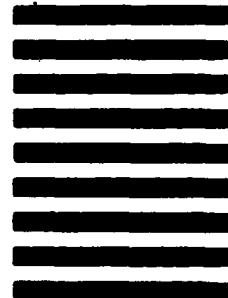


**NO POSTAGE  
NECESSARY  
IF MAILED  
IN THE  
UNITED STATES**

**BUSINESS REPLY MAIL**  
FIRST CLASS PERMIT No 0001, APG, MD

POSTAGE WILL BE PAID BY ADDRESSEE

Director  
U.S. Army Ballistic Research Laboratory  
ATTN: SLCBR-DD-T  
Aberdeen Proving Ground, MD 21005-9989



-----FOLD HERE-----